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### SPATIO-TEMPORAL VARIATIONS OF HEAVY METALS IN Penaeus monodon AND AMIBIENT MEDIA OF COASTAL WEST BENGAL, INDIA

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#### **ABSTRACT**

The present study is an attempt to understand the dynamics of zinc, copper and lead in the muscles, gills and hepatopancreas of Penaeus monodon collected from two different stations in coastal West Bengal namely Jharkhali (Station 1) and Shankarpur (Station 2) in 2017 through four seasons (premonsoon, monsoon, postmonsoon and winter). The former station is located in the central Indian Sundarbans within the mangrove ecosystem and the location of the later station is in Midnapore district of West Bengal and is noted for fish landing activities. The heavy metals in the ambient media (water and sediment) and shrimp tissues followed the order Zn > Cu > Pb. The concentrations of the metals exhibited significant spatial variations and followed the order Shankarpur (Station 2) > Jharkhali (Station 1). The bioaccumulation exhibited significant organ specificity with highest values in hepatopancreas followed by gills and muscles, irrespective of seasons and stations.

#### **KEY WORDS**

Penaeus monodon, heavy metals, coastal West Bengal, muscles, Gills, hepatopancreas

#### **INTRODUCTION**

The estuarine system of the planet Earth is treated as the conveyor belt for transport of dissolved and particulate materials from continents into the oceans. Out of  $250 \times 10^{14}$  g year<sup>-1</sup> of material that enter the ocean from the continents,  $210 \times 10^{14}$  g year<sup>-1</sup> is transported *via* rivers and estuaries [1]. Heavy metal contamination of the environment has been occurring for centuries, but its extent has increased markedly in the last fifty years due to technological developments and increased consumer use of materials containing these metals. Increased circulation of hazardous heavy metals in soil, water and air has raised considerable concern for environmental protection and human health [2].

The rapid industrialization and urbanization of the city of Kolkata, Howrah and the newly emerging Haldia

complex in the maritime state of West Bengal has caused considerable ecological imbalance in the adjacent coastal zone. The Hooghly estuary situated on the western sector of coastal West Bengal receives drainage from the Bagar and Reighland canals which have sewage outlets into the estuarine system. The chain of factories and industries situated on the western bank of the Hooghly estuary is another prominent cause behind the gradual transformation of this beautiful ecotone into stinking cesspools of the mega polis. The lower part of the estuary has multifarious industries such as paper, textiles, chemicals, pharmaceuticals, plastic, shellac, food, leather, jute, tyres and cycle rims [3, 4]. Toxic effluents from these industries might scratch the magnificent network of life spun over a long evolutionary period of time in this biotope. In addition to these, the mushroom growth of hotels, resorts and a



number of unofficial fish landing centres at the Digha-Shankarpur belt (on the extreme western sector of coastal West Bengal) are some prominent negative pressures on the ecological status of the area. The effluents released by these units into the bay contain appreciable amount of Zn, Cu and Pb, from antifouling paints used for conditioning fishing vessels and trawlers, sewage from aquacultural farms along the estuarine stretch and untreated wastes from Haldia port-cumindustrial complex. Heavy metal contamination in aquatic environments is of critical concern, due to toxicity of metals and their accumulation in aquatic habitat. Heavy metals are not biodegradable, and they undergo a global ecological cycle in which natural waters are the main pathways. On this background the present study has been undertaken to analyze the levels of Zn, Cu and Pb in the aquatic phase and underlying surface sediments in two selected stations and Penaeus monodon was selected as candidate species to understand the bioaccumulation of these heavy metals in the biological samples thriving in the study area.

We have considered the Jharkhali area (Station 1) as the control zone for the present study due to minimum anthropogenic disturbances in this station compared to Shankarpur fish landing area (Station 2) where there is a huge crowding of fishing vessels and trawlers.

#### **MATERIALS AND METHODS**

#### Selection of stations

Two sampling sites/stations were selected for the present study. Station 1 (Jharkhali) is located in the mangrove belt of central Indian Sundarbans, while Station 2 (Shankarpur) is a busy fish landing station.

#### Analysis of dissolved heavy metals

Surface water samples were collected in all the four seasons during high tide using 10-l Teflon-lined Go-Flo bottles, fitted with Teflon taps and deployed on a rosette or on Kevlar line, with additional surface sampling carried out by hand. Shortly after collection, samples were filtered through Nuclepore filters (0.4 µm pore diameter) and aliquots of the filters were acidified with sub-boiling distilled nitric acid to a pH of about 2 and stored in cleaned low-density polyethylene bottles. Dissolved heavy metals were separated and preconcentrated from the seawater using dithiocarbamate complexation and subsequent extraction into Freon TF, followed by back extraction into HNO<sub>3</sub> [5]. Extracts were analysed for Zn, Cu and Pb by Atomic Absorption

Spectrophotometer (Perkin Elmer: Model 3030). The accuracy of the dissolved heavy metal determinations is indicated by good agreement between our values and reported for certified reference seawater materials (CASS 2) (Table 1).

Table 1: Analysis of reference material for near shore seawater (CASS 2)

Element	Certified value (µg l <sup>-1</sup> )	Laboratory results (μg l <sup>-1</sup> )
Zn	1.97 ± 0.12	$2.01 \pm 0.14$
Cu	0.675 ± 0.039	0.786 ± 0.058
Pb	$0.019 \pm 0.006$	$0.029 \pm 0.009$

## Analysis of biologically available heavy metals in surface sediment

Sediment samples from surface (1 cm depth) were collected by scrapping using a pre-cleaned and acid washed plastic scale and immediately kept in precleaned acid washed polythene bags, which were sealed. The samples were washed with metal free double distilled water and dried in an oven at 105°C for 5 – 6 hours, freed from visible shells or shell fragments, ground to powder in a mortar and stored in acid washed polythene bags. Analyses of biologically available metals were done after re-drying the samples, from which 1 gm was taken and digested with 0.5 (N) HCl [6]. The resulting solutions were then stored in polythene containers for analysis. The solutions were finally flame aspirated in the Atomic Absorption Spectrophotometer (Perkin Elmer: Model 3030) for the determination of metal concentrations. No detectable trace metals were found in the reagent blank. Analysis of the NIES Sargasso sample was carried out to assure the quality of the data (Table 2).

Table 2: Analysis of reference material (NIES Sargasso sample) for sediments obtained from the National Institute of Environmental Studies, Japan

Element	Certified value (µg g <sup>-1</sup> )	Laboratory results (μg g <sup>-1</sup> )
Zn	28.6	26.2
Cu	14.9	13.7
Pb	2.4	2.9

Analysis of heavy meals in tissues of *Penaeus monodon* 10 gm of samples from the selected organs of the species (*P. monodon*) were dried at 105°C overnight.



Each dried sample (1 gm on dry weight basis) was digested with a mixture of nitric acid and hydrogen peroxide followed by addition of hydrochloric acid. The digested samples were analyzed for Zn, Cu and Pb against standard concentration of each metal on a Perkin Elmer Atomic Absorption Spectrophotometer (Model 3030) equipped with an HGA-500 graphite furnace atomizer and a deuterium background corrector. Blank correction was done to bring accuracy to the results.

The accuracy and precision of our results were checked by analyzing standard reference material (SRM, Dorm-2). The results indicated good agreement between the certified and the analytical values (Table 3).

Table 3: Concentrations of metals found in Standard Reference Material DORM-2 (dogfish muscle) from the National Research Council, Canada (all data as means ± standard errors, in ppm dry wt)

Value	Zn	Cu	Pb	Cd
Certified	26.8	2.34	0.065	0.043
SE	2.41	0.18	0.009	0.005
Observed*	23.9	2.29	0.060	0.040
SE	1.99	0.17	0.006	0.006
Recovery (%)	89.2	97.8	92.3	93.0

#### **RESULTS AND DISCUSSION**

In the present study, metals accumulated in the shrimp muscles in the order Zn > Cu > Pb. Significant spatial variations of metal concentrations in the shrimp muscles were observed between the selected stations, which reflect the adverse impact of industrialization and urbanization on the biotic community. Station 2 needs serious attention as the metal levels in all the shrimp species are considerably higher. The metal levels in the ambient media also exhibited similar picture with higher values in station 2 compared to station 1 (Fig. 1, 2, 3 & 4).

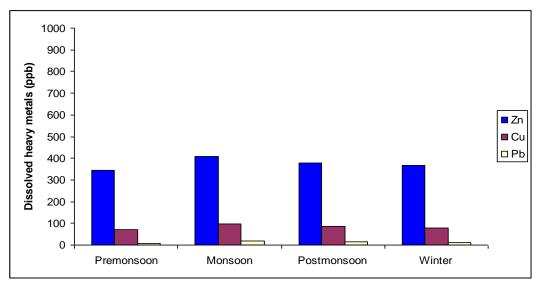


Fig. 1 Seasonal variation of dissolved heavy metals in Station 1 (Jharkhali)



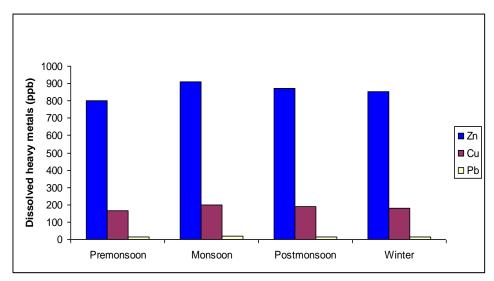


Fig. 2 Seasonal variation of dissolved heavy metals in Station 2 (Shankarpur)

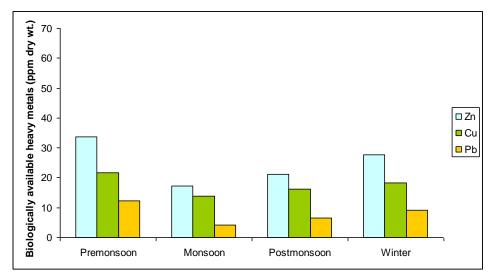


Fig. 3 Seasonal variation of biologically available heavy metals in Station 1 (Jharkhali)

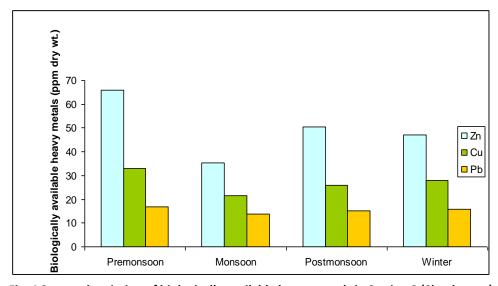


Fig. 4 Seasonal variation of biologically available heavy metals in Station 2 (Shankarpur)



Of the three metals studied in the present work, Zn and Cu are essential elements while Pb is non-essential for most living organisms. The concentrations of zinc and copper in all the shrimp samples were relatively higher, compared to the concentrations of Pb in same shrimp samples. It can be explained because these metals (Cu and Zn) are essential elements required by shellfishes for metabolic processes. Zinc and copper appear to diffuse passively (probably as a soluble complex) by the gradients created through the adsorption of membrane surfaces and are found in blood proteins metallothioneins. Some researchers [7] concluded that different tissues of aquatic animals provide and/or

synthesize non-exchangeable binding sites resulting in different accumulation levels. Further other scientists [8] pointed out that the affiance of metal uptake from contaminated water and food may differ in relation to ecological needs, metabolism, and contamination gradients of water, food, and sediment, as well as other factors such as salinity, temperature, and interacting agents. In this study we also observed a significant organ specificity of metals in the shrimps of the selected stations. All the three metals exhibited highest values in hepatopancreas followed by gills and muscles (Fig. 5-10).

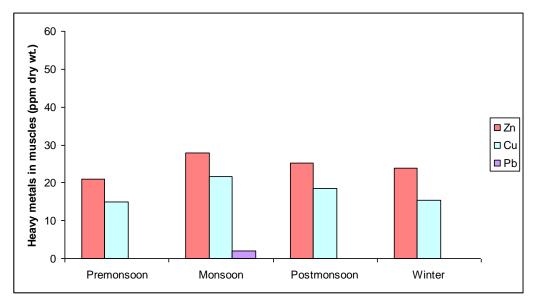


Fig. 5 Seasonal variation of heavy metals in muscles of *P.monodon* in Station 1 (Jharkhali)

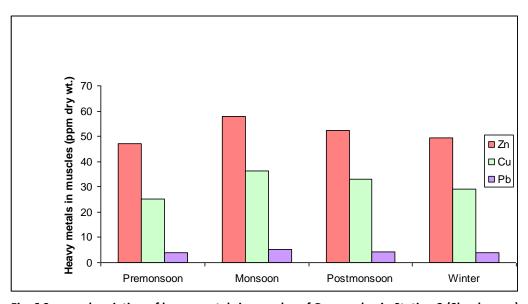


Fig. 6 Seasonal variation of heavy metals in muscles of *P.monodon* in Station 2 (Shankarpur)



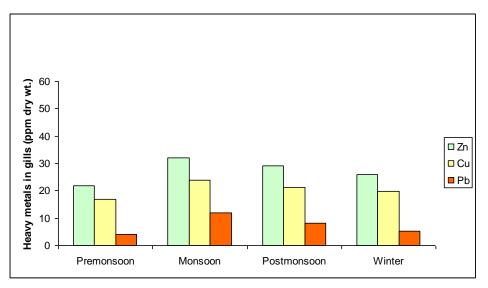


Fig. 7 Seasonal variation of heavy metals in gills of P.monodon in Station 1 (Jharkhali)

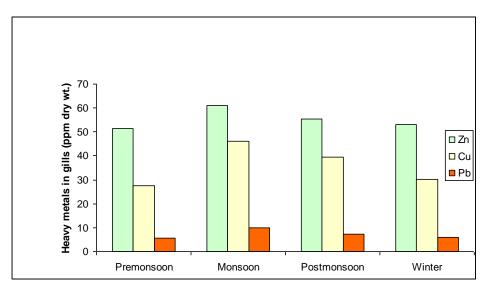


Fig. 8 Seasonal variation of heavy metals in muscles of *P.monodon* in Station 2 (Shankarpur)

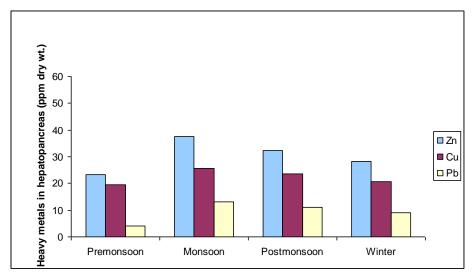


Fig. 9 Seasonal variation of heavy metals in hepatopancreas of *P.monodon* in Station 1 (Jharkhali)



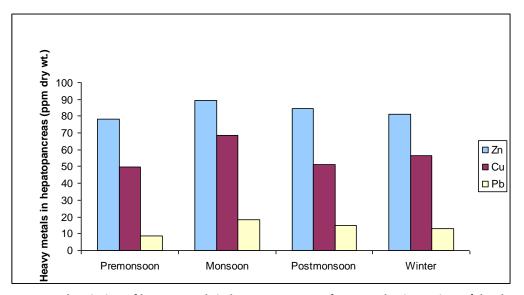


Fig. 10 Seasonal variation of heavy metals in hepatopancreas of P.monodon in Station 2 (Shankarpur)

Metals generally enter the aquatic environment through atmospheric deposition, erosion of geological matrix or due to anthropogenic activities caused by industrial effluents, domestic sewage and mining wastes. From an environmental point of view, coastal zones can be considered as the geographic space of interaction between terrestrial and marine ecosystems that is of great importance for the survival of a large variety of plants, animals and marine species [9]. Adverse anthropogenic effects on the coastal environment include eutrophication, heavy metals, organic and microbial pollution and oil spills [10]. The discharge of these wastes without adequate treatment often contaminate the estuarine water with heavy metals, many of which bioaccumulate in the tissues of resident organisms like fishes, oysters, crabs, shrimps, seaweeds etc. In many parts of the world, especially in coastal areas and on smaller islands, shellfish is a major part of food, which supplies all essential elements, required for life processes in balanced manner [11]. In developing countries like India, the demand for protein is accelerating at a rapid rate. The annual per capita fish consumption in India is only 4 kg against the recommended 31 kg by the Nutritional Advisory Committee on human nutrition.

#### **CONCLUSIONS**

In the present study the relatively higher values of heavy metals in the ambient media and tissues of *P.monodon* in Station 2 (Shankarpur) may be attributed to the existence of busy fish landing station in this area. Large

number of fishing vessels and trawlers use anti-fouling paints preferable during dry docking as a part of routine conditioning of these systems to avoid the settlement of barnacles, oysters and seaweeds on them. These antifouling paints are the sources of heavy metals in the ambient water and sediments, which is practically very less in Station 1 (Jharkhali). The presence of dense mangrove vegetation in Jharkhali is also another reason for lower levels of these heavy metals in the ambient media and biological samples as these mangrove floral species have unique potential to biopurify the environment through the process of bioremediation [4,12]. Thus, large scale plantation of mangroves is a cost-effective method to minimize the levels of heavy metals in highly contaminated areas of estuaries and bays as seen in case of station 2 (Shankarpur) in the present study.

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